Electrochemistry in Thin Layers of Solution

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Although the major recent interest in the potentialities of thin layer electrochemical experiments seems to date from a paper published in 1963 (1), the idea that advantages might be inherent in experiments with very

(1) C. R. Christiansen and F. C. Anson, Anal. Chem., 35, 205 (1963).

thin layers of solution is older. In 1962, Schmidt and Gygaux (2), for example,

(2) G. Schmidt and H. R. Gygaux, Chimia, 16, 165 (1962).

discussed the use of a thin layer cell for studies of metal deposition on solid electrodes and presented designs for useful cells.

However, the advent of a micrometer-type thin layer cell (3,4)

(3) A. T. Hubbard and F. C. Anson, Anal. Chem., 36, 723 (1964).

(4) D. M. Oglesby, S. H. Omang, and C. N. Reilley, ibid., 37, 1312 (1960).

has made the exploitation of the technique much easier and, therefore, more rapid.

Figure 1 shows a typical morcometer-type cell. The details of its construction and operation have been given (3,4) and need not be repeated here. Descriptions of numerous experimental applications of this type of cell have also appeared (5-13) as well as an impressive catalog of suggested experiments for

(5) A. T. Hubbard and F. C. Anson, J. Electroanal. Chem., 9, 163 (1963).

(6) A. T. Hubbard and F. C. Anson, Anal. Chem., 38, 58 (1966).

(7) Ibid., 38, 692 (1966).

(8) Ibid., 38, 1601 (1966).

(9) Ibid., 38, 1887(1966).

(10) D. M. Oglesby, L. B. Anderson, B. McDuffie, and C. N. Reilley, ibid., 37, 1317 (1966).

(11) L. B. Anderson and C. N. Reilley, J. Electroanal. Chem., 10, 295 (1965).

(12) H. Dahms, ibid., 11, 62 (1966).

(13) D. M. Ogelsby, J. D. Johnson, and C. N. Reilley, Anal. Chem., 38, 385 (1966).

which the results have been predicted if not yet obtained. (14,15)

(14) L. B. Anderson and C. N. Reilley, J. Electroanal. Chem., 10, 538 (1965).

(15) L. B. Anderson, B. McDuffie and C. N. Reilley, ibid., 12, 477 (1966).

One of the major unique advantages of the thin layer approach is the facility it provides for performing fast exhaustive electrolysis. The dimensions of the thin layer can be made small enough so that all of the reactant dissolved in the solution reaches the electrode surface by diffusion within a few seconds. Under these conditions all of the reactant contained in the layer of solution is electrolized so that the relation between the amount of electricity, Q required to consume all of the reactant and its concentration, C, is given by Faraday's Law:

$$Q = nFA\ell C \tag{1}$$

where n is the number of electrons involved in the electrode reaction, F is the Faraday, A is the electrode area, and ℓ is the solution thickness (A × ℓ = the solution volume).

Excellent agreement of experimental results with equation 1 have been obtained and advantage has been taken of this property to determine n-values for electrode reactions.

A particularly simple and yet powerful exploitation of the adherence of thin layer experiments to equation 1 is in studies of reactant adsorption (4). If the faces of the electrodes in the micrometer cell are equilibrated with an excess a solution of potentially adsorbed reactant and then all of the solution except for a thin layer of volume A × ℓ removed, and an exhaustive electrolysis performed the quantity of electricity required will be given by equation 2

$$Q = nFA\ell C + 2nFA\Gamma \tag{2}$$

where Γ is the amount of adsorbed reactant in moles/cm² and the factor of 2 arises because the adsorption occurs on two electrodes of area A. In favorable cases it is possible to make ℓ so small that $2nF\Gamma$ is comparable or even greater than $nFA\ell C$ so that quite accurate measurements of Γ are possible.

Another already exploited use of the thin layer cell is in the detection of intermediates in electrode reactions. By insulating the two platinum pole pieces of the thin layer cell from each other they can be used as independent probes of the same thin layer of solution. Thus, products of a reaction at one electrode can be continuously detected and determined at the opposing electrode which can be independently controlled at whatever potential is characteristic for the determination of particular suspected intermediate.

Advantage has been taken of this feature of thin layer cells to establish that oxygen is not evolved in significant amounts when platinum electrodes are oxidized at potentials below 1.2 volts vs S. C. E. and that considerable ozone is evolved at more anodic potentials (15). It has also been possible by means of the

(15) G. Lauer, Ph. D. Thesis, California Institute of Technology, Pasadena, California, 1966.

thin layer cell to detect directly the presence of "irreducible oxide" on the surface of platinum electrodes which have been oxidized and subsequently reduced. When the thin layer electrodes were treated in this way and then just filled with warm hydrochloric acid, current-potential curves were obtained which matched those

for independently prepared solutions of $PtCl_6^=$. Blank experiments with oxidized, reduced, and "aged" electrodes did not lead to any detectable $PtCl_6^=$ (15).

Reilley and co-workers have applied the thin layer approach to twin electrode cells in which one face of a micrometer electrode is an anode and the other a cathode. Steady state currents can be set up with such a configuration and the magnitudes of these currents can be used to measure diffusion coefficients or to study the kinetics of chemical reactions coupled to the electrode reaction. The great simplification in mathematics afforded by the thin layer conditions permits the straightforward treatment of cases that pose considerable difficulty with the usual techniques, e.g. the second order disproportionation of uranium(V) (16).

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(16) C. N. Reilley and B. McDuffie, Anal. Chem., **38**, 1881, (1966).

The list of other potential uses for the thin layer approach is endless and depends only on the ingenuity of the experimenter and his success at constructing improved cells. Especially high on our priority list are the construction of an effective mercury thin layer cell and applications to solutions containing little or no supporting electrolyte.
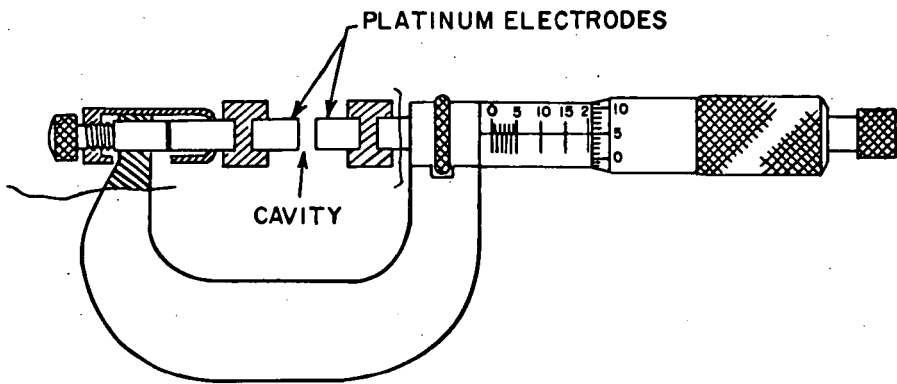
PLATINUM ELECTRODES

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Figure 1 - Micrometer - type
Thin Layer Cell